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Studies on influence of process parameters on simultaneous biodegradation of atrazine and nutrients in aquatic environments by a membrane photobioreactor

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ABSTRACT

A Lab scale algal-bacterial membrane photobioreactor (MPBR) was designed and operated under 12-h light and 12-h dark conditions with a light intensity of 8000 lx, in order to investigate the effects of initial concentrations of atrazine, carbon concentration, and hydraulic retention time on the ability of this photobioreactor in simultaneous removal of atrazine and nutrients in the continuous mode. The removal efficiencies of atrazine (ATZ), chemical oxygen demand (COD), phosphorus ($\text{PO}_4^{3-}\text{-P}$) and nitrogen (NO_x) in optimum condition was more than 95%, 99%, 98% and 97% when the maximum removal rates were 9.5×10^{-3} , 99.231, 11.773 and 7.762 mg/L-day, respectively. Results showed that the quality of the effluent was reduced by the increase of atrazine concentration. The outcomes on the hydraulic and toxic shocks indicated that the system has a relatively good resistance to the shocks and can return to the stable conditions. Microalgae showed a great deal of interest and capability in cultivating and attaching to the surface of the membrane and bioreactor, and the total biomass accumulated in the system was greater than 6 g/L. The kinetic coefficients of atrazine removal were also studied using various kinetic models. The maximum atrazine removal rate was determined by the modified Stover-Kincannon model. The results approved the ability of the MPBR reactor in wastewater treatment and microalgae cultivation and growth. The decline of atrazine concentration in this system could be attributed to the algal-bacterial symbiosis and co-metabolism process. Accordingly, the MPBR reactor is a practical, simple, economical and therefore suitable process for simultaneous biodegradation of chlorinated organic compounds and nutrients removal from aquatic environments.

1. Introduction

On-growing enhancement of the human population has produced a large amount of municipal, industrial, and agricultural wastewater throughout the world. Uncontrolled entry of such wastewater into the environment leads to a gradual decrease in the quality of water

resources. In this regard, the development of social concerns for the conservation of natural water resources has led to the development of strict rules regarding the necessary treatment before discharging of wastewater in environment and the development of various types of treatment methods (Accinelli et al., 2012; Derakhshan et al., 2017b, 2016b; Metcalf and Eddy, 1991; Ghaneian et al., 2017). However,

Abbreviations: ATZ, atrazine; COD, chemical oxygen demand; DO, dissolved oxygen; EPS, extracellular polymeric substances; HPLC, high performance liquid chromatograph; HRT, hydraulic retention times; MPBR, membrane photobioreactor; MF, microfilter; OD, optical density; PVDF, polyvinylidene fluoride; SEM, scanning electron microscopy; SRT, solids retention time; TMP, transmembrane pressure

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Nomenclature

B_{ATZ}	Volumetric atrazine loading (g_{ATZ}/m^3 d).
C_e	Atrazine concentrations in the effluent (g/m^3).
C_i	Atrazine concentrations in the influent (g/m^3).
HRT	Hydraulic retention time (day or hour).
k_1	First order kinetic constant (1/d).

k_s	Half saturation constant (g/m^3).
Q	Inflow rate (m^3/d).
r_{ATZ}	Volumetric atrazine removal (g_{ATZ}/m^3 d).
r_{max}	Maximum substrate removal rate (g_{ATZ}/m^3 d).
S	Effluent substrate concentration (g/m^3).
S_0	Influent substrate concentration (g/m^3).
V	Reactor volume (m^3).

conventional wastewater treatment methods such as the use of active sludge and anaerobic digestion pools are subject to severe technical, economic, and environmental constraints due to the high energy consumption, high cost, and low efficiency. In addition, conventional wastewater treatment methods have the following disadvantages: 1) loss of nutrients (i.e. N, P), 2) low removal efficiency of nutrients, 3) high operational costs of conventional wastewater treatment and 4) secondary products and byproduct produced during the conventional wastewater treatment. Hence, the use of algae for the biological treatment of wastewater, nowadays, has been recognized as a global strategy (Boelee et al., 2011; Butler et al., 2016; Grady Jr. et al., 2011; Metcalf and Eddy, 1991; Wu et al., 2016). Microalgae have been used in large ponds for the treatment of wastewater for a long time. One of the most important limitations of microalgae systems application during treatment processes is the recovery and separation of microalgae from treated effluent streams. Among the solutions to deal with this problem, the technique of microalgae immobilization has been considered dramatically. Some benefits of this method include providing a suitable media for the maintenance active cells in the treatment process, which leads to an increase in cell retention time within the bioreactor. Algal biomass accumulated in photobioreactors can also be used for the production of methane, compost, animal feed, and liquid biofuels. In these systems, discharge of the evacuated effluent into the environment is expected, without microalgae separation from the aqueous environment. Today's attention to the use of microalgae in wastewater treatment processes is because of the interests in the field of biofuels production as a vital and sustainable economic practice when wastewater is used as a source of energy and nutrients for microalgae growth and cultivation. Since microalgae-based wastewater treatment systems require extensive land and space, efforts have been made to improve these systems by resorting to ultra-compact systems. Biofilm systems and increasing microalgae attached growth enable them to keep the biomass in abundance during short periods of Hydraulic Retention Times (HRTs). Since mixing is not needed during these processes, energy consumption and costs are going to be reduced (Gao et al., 2016; Luo et al., 2017; Maza-Márquez et al., 2017; Novoveská et al., 2016).

Biological wastewater treatment is usually performed by the aerobic and anaerobic processes as though their discharged effluent still contains inorganic compounds such as nitrate, ammonium, and phosphate ions that can contaminate water resources. This leads to an algal blooming, non-ionized ammonia toxicity for fishes and other aquatic organisms, and interference with disinfection process when free residual chlorine is needed (Metcalf and Eddy, 1991). Conley et al. (2009) believe that P and N are key factors in the occurrence of eutrophication, so further treatment would be necessary to prevent the occurrence of this phenomenon in aquatic environments. Removal of nutrients such as N and P to very low levels from the wastewater by microalgae is much considered due to the benefits of producing valuable biomass, recycling nutrients, simple technology, high efficiency, and low costs. For this reason, it is one of the most suitable and sustainable alternative to post-treatment systems such as denitrifier filters that require an organic carbon source and emit CO_2 (Boelee et al., 2011; Gao et al., 2014; Metcalf and Eddy, 1991). Microalgae bio-systems are proposed as an excellent and efficient solution for secondary treating because they are able to use inorganic N and P for growing and remove heavy metals. Recently, a new combination with a submerged membrane module

allowing independent control of the hydraulic time, has been investigated. Consequently, the microalgae growth and cultivation and the efficiency of nutrient removal from the wastewater can occur simultaneously, which is useful for the production of microalgae biomass and also nutrients removal (Boonchai and Seo, 2015; Gao et al., 2015; Luo et al., 2017; Maza-Márquez et al., 2017).

The use of pesticides such as atrazine have increased due to the lack of agricultural land, increasing numbers of people that drive up the food demand, and the products loss by pests. Because of low vapor pressure, long half-life in soil, and high mobility, atrazine has contaminated various ecosystems (Baghapour et al., 2013; Derakhshan et al., 2016a; Nasseri et al., 2014). Atrazine's toxicity belongs to the class III according to United States Environmental Protection Agency (EPA); however, its importance cannot be denied due to the related risk for groundwater contamination. The amount of atrazine used in agriculture has increased significantly in recent decades, resulting an unbelievable growth in the pollution of aquatic and terrestrial environment, and eventually the release of aromatic pollutants. Selected technologies for atrazine removal dependent on many factors such as atrazine concentration, other pollutants concentration in the environment, process and operational conditions, or system economic aspects. The application of physicochemical technologies such as absorption, UV oxidation, etc to eliminate atrazine typically results in the production of intermediate or final dangerous products. A sustainable economic and environmental approach compared to physical/chemical methods is bioremediation widely used by resorting to microorganisms' activities (Baghapour et al., 2013; Boopathy, 2017; Wen et al., 2016).

The aim of this study was to evaluate the performance of an algal-bacterial biofilm reactor as a post-treatment system for the simultaneous removal of COD, nutrients, and atrazine (as a model of chlorinated herbicide compounds widely used in agriculture) from aquatic environments. Furthermore, special attention has been paid to the capacity of this system for the aforementioned parameters and the involved factors in exploitation of it in different operational conditions and finally to obtain the final effluent concentration.

2. Material and methods

2.1. Chemicals

All of the chemicals used in this study were purchased from the Merck or Sigma-Aldrich companies with an analytical grade. The standard of prepared atrazine had a purity of 99.9%. Atrazine stock solution was prepared in methanol at a concentration of 1 mg/100 ml. Then, the stock solution was passed through a 0.22 μm filter and stored at $-18^\circ C$. Subsequently, a serial dilution was used to calibration the High Performance Liquid Chromatograph (HPLC). The solutions were prepared at required concentrations when needed and stored at $-18^\circ C$ for a period of less than 3 months. The desired solutions were prepared by dissolving the required amount of chemicals in the deionized water. Apart from the atrazine, all solutions were autoclaved at $120^\circ C$ for 20 min and then stored at $4^\circ C$. All the prepared solutions were kept separately to prevent sediments formation (Derakhshan et al., 2017a, 2016a, 2017b).

2.2. Preparing and Start-up the photobioreactor

In this study, the effect of influent's atrazine concentration, HRT, and COD concentration were evaluated in a Lab scale membrane photobioreactor. As shown in Fig. 1, a cylindrical MPBR reactor made of plexiglas (diameter = 20 cm, height = 30 cm, freeboard = 5 cm) was used. Total and working volumes of the reactor were 9.4 and 5 L, respectively. A polyvinylidene fluoride (PVDF) hollow-fiber microfilter (MF) membrane module that used as a solid-liquid separator was submerged in the middle of the reactor. PVDF membrane with an average pore size of 0.1 μm was used. The effective surface area was 0.043 m^2 and the maximum flux from the membrane was equaled 20 $\text{L}/\text{m}^2 \text{ h}$. Membrane permeate was intermittently withdrawn by suction pumps, which operated in 3 min on/ 12 min off cycle. The lighting was provided by 5 red/blue LED lamps with a ratio of 1/4, with a power of 9 w. These lamps were located on top and side walls (at a distance of 5 cm from the surface) of the photobioreactor and they were used throughout the day for 12 h. For the entire duration of the experiments, the maximum light intensity on the surface of the reactor was about $8000 \pm 9.7 \text{ lx}$, which was measured at the surface of the mixed liquid within the photobioreactor. An air compressor was used to provide aeration and mixing effect (0.04% of the used air contained CO_2 for aeration). On the bottom of the bioreactor, a diffuser was installed. For injection of the influent flow a peristaltic pump was applied. Daily care was taken to ensure membrane function and biofilm formation. The transmembrane pressure (TMP) was continuously monitored when the membrane flow was set at a maximum level. When the amount of TMP levels exceeds recommended maximum permissible levels (30 kpa), the membrane module was removed from the system for physical washing and cleaning. The membrane module was washed with distilled water for 30 min and submerged again in the photobioreactor. Initial MPBR seeding was prepared by the microalgal-bacterial seed collected from the wastewater treatment ponds located in Foladshahr, Isfahan Province, with the initial biomass concentration of $71.34 \pm 5.29 \text{ mg/L}$ and it used for more than 180 days at ambient temperature ($26 \pm 3^\circ\text{C}$). In the present work, synthetic wastewater was used in order to eliminate the interfering factors, to control the fluctuations in the wastewater, and to monitor the system better. The pH of the influent wastewater was adjusted at about 7 ± 0.3 by sodium bicarbonate at a concentration of 0.5 mol/L (Derakhshan et al., 2017a, 2016a, 2017b). The water needed to prepare synthetic wastewater was provided by the tap water. The composition of the synthetic wastewater was as follows: 30 mg/L $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, 20 mg/L NaHCO_3 , 15 mg/L NaNO_3 , 5 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 5 mg/L KH_2PO_4 , 5 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.2 mg/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.001 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.2 mg/L H_3BO_3 , 0.5 mg/L MnSO_4 , 0.2 mg/L $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. Trace elements and vitamins: 0.1 mg/L EDTANa₂, 1.81 mg/L $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.22 mg/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.39 mg/L $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.08 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.05 mg/L $\text{Co}(\text{NO}_3)_2$, 0.1 mg/L vitamin B1, $5 \times 10^{-4} \text{ mg/L}$ vitamin H, $5 \times 10^{-4} \text{ mg/L}$ vitamin B12 (Baghapour et al., 2013; Boelee et al., 2011; Gao et al., 2016). According to the previous studies, it has been determined that the maximum biological removal efficiency of atrazine occurs at 32°C . The temperature of the wastewater entering the feeding tank was therefore controlled by an electric heater at 32°C . Although the synthetic wastewater ingredients were completely dissolved in water, but a small submerged pump was used to return the wastewater from the floor to the reservoir surface every 15 min to prevent the change in the wastewater quality (Derakhshan et al., 2016a, 2017b). The MPBR reactor was initially fed and tested with synthetic wastewater (Table 1) for starting the biological adaptation phase. Synthetic wastewater contained the required micronutrients, based on BG11 culture medium, to control the restriction role of any nutrient except N and P. After 132 days of the continuous running, we used real secondary effluent of Shiraz wastewater treatment plant. Before entering the real secondary effluent to the system, pre-treatment was performed on it that is, the secondary effluent was allowed to settle during the night and then, the

upper layer of the liquid was used as an influent to system. Characteristics of the synthetic wastewater and pre-treated wastewater are given in Table 2. The start-up of the MPBR photobioreactor was performed by the setup phase for the purpose of biological adaptation and acclimazation of the microorganisms to the environmental conditions. To prevent microalgae growth outside of the photobioreactor, all hoses were in black, all used dishes were dark brown and their outer walls covered with foil, and all dishes were autoclaved before usage. The HRT was adjusted by means of the influent's flow rate control. To discharge the possible accumulated sludge, a drain valve was used at the bottom of the bioreactor. To obtain a high degree of the microorganism's adaptation to the atrazine, the reactor was fed with synthetic wastewater with a volume of 5 L containing 0.01 mg/L of atrazine. The effluent from the reactor was re-circulated to the influent. The concentration of atrazine was also monitored in the effluent. It has been assumed that when atrazine removal efficiency exceeds 90%, the microbial adaptation step has been completed. In order to concentrate and increase the microbial population capable of atrazine degradation, the solution was discharged from the reactor and the reactor was re-fed with a fresh nutrition solution containing 0.01 mg/L of atrazine and effluent was returned to the influent using the above-mentioned method. This phase was repeated 3 times to ensure the increase of the microbial population. This phase lasted 44 days. In order to increase the accuracy, enhance the performance, and eliminate the effect of the interfering factors, the primary microorganisms inoculated into the photobioreactor as seed were grown in completely identical conditions using a glass container (control experiment).

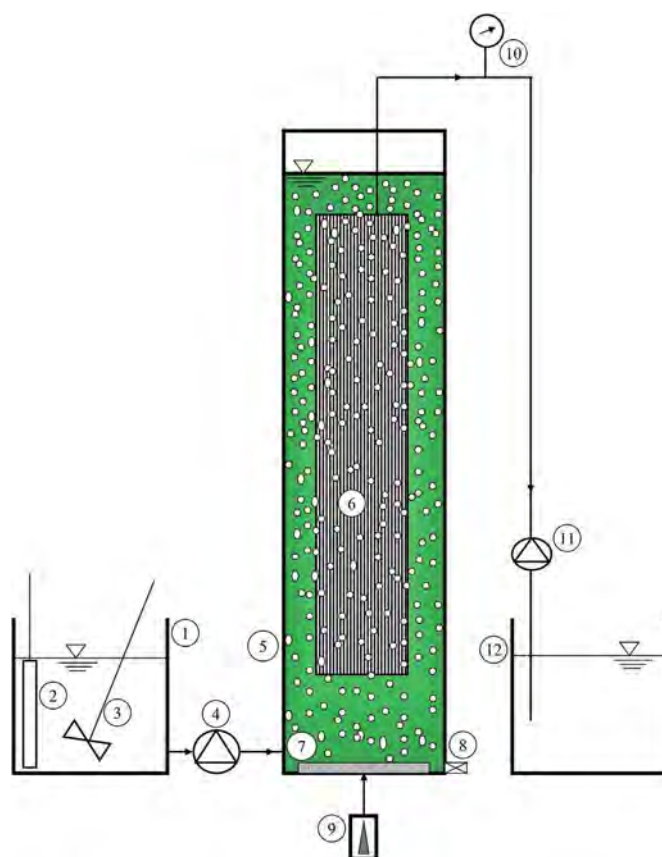


Fig. 1. Schematic diagram of the Photobioreactor. 1. Reservoir of feedstock, 2. Electric heater, 3. Electric mixer, 4. Peristaltic pump, 5. Photobioreactor, 6. Submerged membrane, 7. Diffuser, 8. Discharge sludge port, 9. Air compressor, 10. Gauge, 11. Suction pump, 12. Reservoir of outlet.

Table 1
Operating parameter and removal efficiency in the microalgal-bacterial MPBR system.

	Synthetic wastewater effluent							Real secondary effluent	
	Start-up	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6	Phase 7	
Operating period (d)	0 – 44	45 – 54	55 – 76	77 – 106	107 – 114	115 – 120	121 – 132	133 – 147	
Influent ATZ (mg/L)	$0.01 \pm 1 \times 10^{-4}$	$0.01 \pm 1 \times 10^{-4}$	$0.05 \pm 1 \times 10^{-3}$	$0.1 \pm 1 \times 10^{-3}$	$0.01 \pm 1 \times 10^{-4}$	$0.01 \pm 1 \times 10^{-4}$	$0.01 \pm 1 \times 10^{-4}$	$0.028 \pm 1 \times 10^{-4}$	
Influent COD (mg/L)	30 ± 0.7	30 ± 0.8	30 ± 0.2	30 ± 0.8	30 ± 0.6	50 ± 1.2	100 ± 1.7	48 ± 0.5	
Influent PO ₄ ³⁻ (mg/L)	12 ± 0.9	12 ± 0.2	12 ± 0.4	12 ± 0.6	12 ± 0.1	12 ± 0.6	12 ± 0.4	9.26 ± 0.7	
Influent NOx (mg/L)	8 ± 0.6	8 ± 0.1	8 ± 0.2	8 ± 0.5	8 ± 0.6	8 ± 0.9	8 ± 0.7	9.85 ± 0.6	
ATZ removal (%)	< 90 ± 0.9	94.8 ± 0.3	94.2 ± 0.4	89.1 ± 0.1	95.2 ± 0.4	90.2 ± 0.3	87.6 ± 0.2	89.1 ± 0.1	
COD removal (%)	< 95 ± 6.7	96.3 ± 0.4	97.1 ± 0.1	90.8 ± 0.4	97.3 ± 0.2	98.1 ± 0.2	99.2 ± 0.3	97.5 ± 0.4	
PO ₄ ³⁻ removal (%)	< 94 ± 4.7	93.9 ± 0.2	95.1 ± 0.4	91.4 ± 0.3	94.4 ± 0.1	97.3 ± 0.1	98.1 ± 0.4	95.1 ± 0.2	
NOx removal (%)	< 94 ± 6.1	91.1 ± 0.1	94.9 ± 0.2	88.8 ± 0.3	92.5 ± 0.2	95.7 ± 0.3	97.1 ± 0.2	94.8 ± 0.1	
Mixed liquor pH	7.8 ± 0.8	7.0 ± 0.3	6.8 ± 0.2	7.1 ± 0.4	6.9 ± 0.1	7.2 ± 0.3	7.4 ± 0.1	7.2 ± 0.3	

2.3. Experimental protocol

The Effects of the Atrazine's influent concentrations (0.01 up to 0.1 mg/L), COD (30 – 100 mg/L) and HRT (6–24 h) were investigated on the performance of the MPBR reactor regarding atrazine biodegradation. In each phase of the experiment, the bioreactor was operated until the steady-state situation was achieved. The operation was continued for 3–5 times. It was presupposed that steady-state condition is attained when standard deviation of atrazine removal efficiency remain below 2%. The HRT of 24, 12, and 6 h were considered in the current study for removing target contaminants. After microbial adaptation and enrichment, the continuous phase was launched by feeding with the synthetic wastewater containing 0.01 mg/L atrazine and COD 30 mg/L at an HRT of 24 h. The concentrations of COD, as well as influent and effluent atrazine concentration, PO₄³⁻-P and NOx, were monitored on a daily basis. After achieving steady-state conditions in each phase, sampling was picked-up and parameters such as concentrations of influent and effluent atrazine, COD, PO₄³⁻, NOx, pH (by electrochemically measured (Model F-22, Horiba)), DO (by DO meter (HACH)) and temperature (by Thermometer) was investigated. The COD was colorimetrically determined (Model DR 5000 Spectrophotometer, HACH) following dichromate digestion. Within each phase, sampling was conducted from the two influent and effluent points of the reactor and the tests were repeated at least twice. Samples taken from the effluent and influent were initially centrifuged to remove the suspended solids and then filtered through a cellulosic paper filter with a pore size of 0.45 µm, and the filtrate was subsequently analyzed. The mean of the obtained data was then calculated. Unless otherwise specified sampling method and tests' implementation were performed according to the guidance provided by standard methods for the examination of water and wastewater (APHA, 2005). Samples were analyzed for NOx and PO₄³⁻ with Ion Chromatography (IC) (Metrohm Compact IC 761 equipped with a conductivity detector, using the pre-column Metrohm Metrosep A. Supp 4/5 Guard and the column Metrohm Metrosep A Supp 5, 150/ 4.0 mm). Atrazine was extracted from samples by the Solid Phase Extraction (SPE) method proposed by Ghosh and Philip (2004). Also, to check the buildup and absorption of atrazine in biofilms, the recommended technique by Baghapour et al. (2013) was utilized. A brief explanation is brought in the Supplementary data. Biofilm formed on the membrane media was investigated by the Scanning Electron Microscope (SEM) (model JSM-5800, JOEL, Japan). At the end of the experiments, a small piece of the membrane that biofilm grown on it was cut and then it was slowly washed 3 times with phosphate buffer solution. First, biofilms had been fixed for 2 h at the room temperature with usage of glucocorticoid (2.5 Wt solution) after which lightly washed with phosphate buffer solution (137 mM NaCl, 2.7 mM KCl, 10 mM Na₂HPO₄, 2 mM KH₂PO₄, pH 7.5) for 3 times. Second, 30%, 50%, 70%, 85%, and 100% (v/v) ethanol was used to sequentially dehydrate the fixed samples for 15 min. Third, ethanol within the dehydrated samples was exchanged by isoamyl acetate within 20 min for two times. After these processes, samples have been frozen at –20, –40, –80 °C for 4 h, respectively, and then freeze dried for 12 h. Subsequently, the dried samples had been sputter coated with a thin gold layer for the observation of surface morphology (Derakhshan et al., 2017a, 2017b).

During the startup phase, chlorophyll microalgae concentrations were daily measured in order to determine the amount of biomass production. After extraction, the total microbial lipid content was measured by methanol using the gravimetric method. The existing carbohydrate within the biomass was extracted with a sulfuric acid solution and it was measured by phenol/sulfuric acid. The protein was extracted using sodium hydroxide (0.1 M) and measured using the Lowry's method. Details about the method of extracting and measuring the total content of lipids, proteins, and microalgae carbohydrates have been mentioned in other papers (Gao et al., 2015). In addition, chlorophyll content was measured after its extraction by 90% methanol at

Table 2

Wastewater quality data from the synthetic and real secondary wastewater effluent before and after overnight settling.

Parameters	Synthetic wastewater	Raw real secondary effluent	real secondary effluent after settling
COD (mg/L)	30 ± 3 – 100 ± 5	51 ± 9	48 ± 0.5
ATZ (mg/L)	0.01 ± 1 × 10 ⁻⁴ – 0.1 ± 8 × 10 ⁻⁵	0.03 ± 1 × 10 ⁻⁴	0.028 ± 1 × 10 ⁻⁵
PO ₄ ³⁻ -P (mg/L)	12 ± 0.7	10 ± 1	9.36 ± 0.3
NOx (mg/L)	8 ± 1.2	11 ± 0.8	9.85 ± 0.4
pH	7 ± 0.3	7.6 ± 1.1	7.4 ± 0.7

4 °C for 48 h using a spectrophotometer (Praveen and Loh, 2016b). Suspended microalgal biomass concentration was measured by optical density (OD) in a mixed liquid at 540 nm with an UV/Vis spectrophotometer. The obtained OD was used to calculate the biomass concentration in formula: dry cell weight (mg/L) = 542 × OD₅₄₀ (Praveen and Loh, 2016a). The overall removal efficiency and the rate of target contaminants removal were calculated based on the concentration difference between effluent and influent of the bioreactor.

2.4. Operation

After successful adaptation and microbial population enrichment, the continuous operation phase of the reactor was started by feeding a synthetic wastewater containing 0.01 mg/L of atrazine at the HRT of 24 h. Concentrations of COD, PO₄³⁻, NOx, and influent and effluent atrazine were monitored daily. After startup phase and microbial adaptation, the effects of influent atrazine concentrations (0.01–0.1 mg/L), HRT (6–24 h), and influent COD on the MPBR reactor performance was evaluated concerning simultaneous removal of COD, PO₄³⁻, NOx, and atrazine biodegradation. At each phase, the bioreactor was operated until steady state condition was achieved and the operation continued for three times. In the current research, it was assumed that the stability conditions were obtained when the standard deviation (SD) of atrazine removal efficiencies is less than 2%. Here, HRT of 6, 12 and 24 h were considered to remove target pollutants. In addition, three levels of COD, including 30, 50 and 100 mg/L were taking into account to evaluate the effect of carbon source on MPBR reactor. In order to assess the behavior and power of the photobioreactor in a wide range of loadings, the effect of membrane photobioreactor performance on the atrazine biodegradation was investigated at different concentrations and various HRTs.

3. Results and discussion

3.1. MPBR operation

The operation of the membrane photobioreactor was initiated with the microbial startup and adaptation phase. On the 45th day, capability of the photobioreactor was studied in different phases, summarized in Table 1. After reaching the steady-state conditions at each phase, three levels of COD concentrations (30, 50, and 100 mg/L) and three levels of atrazine concentrations (0.01, 0.05, and 0.1 mg/L) at HRT of 24 h were tested. Fig. 2 indicates the concentration variation of the target pollutants during 147 days of operation. The removal efficiency from the photobioreactor are also shown in Fig. 2. The results of atrazine removal during the startup phase with atrazine concentration of 0.01 mg/L, COD concentration of 30 mg/L, and HRT of 24 h are shown in Fig. 2. As it is clear from Fig. 2, the atrazine, COD, PO₄³⁻ and NOx removal efficiency reached 5.5%, 10.7%, 17.8% and 21.7%, respectively, 1 day after the reactor startup. As it can be seen in Fig. 2, atrazine and organic matter decreased from the influent in all of the applied acclimation runs on the first day after entering into the reactor. This result can be attributed to the dilution by the wastewater inside the bioreactor. Results of the acclimation phase is summarized in Table 3. By increasing the operating time (about 14 days after startup), the efficiency of target

pollutant removal improved and reached to a nearly constant and stable level i.e. more than 91%, indicating the success of the tested system. During the startup, the algal-bacterial biomass began to increase on the biological membrane, which was accompanied by a slight decrease in atrazine, COD, PO₄³⁻ and NOx. As the algae-bacteria increased, the effluent concentrations dropped and eventually reached to a stable level. The concentration of NOx in the wastewater (Fig. 2d) remained constant at 0.37 mg/L after 9 days of operation while the efficiency of removal was more than 94%. Nevertheless, a decreasing trend of the atrazine, COD and PO₄³⁻ was observed and finally reached to 8.5 × 10⁻⁴ mg/L, 0.21 mg/L and 0.36 mg/L respectively, on the 14th day. At the startup phase without removing biomass from the system, the suspended microalgal biomass concentration increased steadily from 71.34 ± 5.29 mg/L to 473.52 ± 2.31 mg/L on the 44th day. During the early stages of the experiments, the function of the system was poor and highly unstable due to the low concentration of biomass in the photobioreactor as well as the presence of persistent toxic compounds; however, the activity of microalgae increased. After the startup phase, the concentration of atrazine was 0.01 mg/L at HRT of 24 h (Phase 1). During the changes in the atrazine concentration, the bioreactor was operated until a steady-state condition in the efficiency of atrazine removal was obtained and then the concentration increased again. The efficiency of contaminants removal profile during abrupt changes of atrazine is shown in Fig. 2. It is apparent that when the concentration of influent atrazine to photobioreactor suddenly increased from 0.01 to 0.05, the removal rates of atrazine and other pollutants were rapidly reduced by 70% one day after the shock. However, the bioreactor function was re-increased with ascending trend about 21 days after the change and returned to stable level removal of more than 90%. On the 77th day, the concentration of influent atrazine was increased up to 0.1 mg/L (Phase 3). With respect to the results and the data shown in Fig. 2, the removal efficiencies of target pollutants in the MPBR photobioreactor reduced sharply one day following the atrazine concentration increase by 77%. Although when atrazine reduced to a concentration of 0.01 mg/L, the reactor performance began to improve and enhanced quickly to the previous levels of removal. Using algae-bacterial biofilms to reduce the amount of organic matter contaminated is a simple operational process that consumes energy from the sunlight and is based on the symbiosis between microalgae and bacteria. In this symbiosis, the oxygen produced by algae during the photosynthesis process is used by the bacteria in the oxidation of organic matters in the environment, and CO₂ produced by bacterial respiration is used by algae during the photosynthesis process (Gao et al., 2016; Luo et al., 2017; Maza-Márquez et al., 2017; Novoveská et al., 2016). According to literature, microalgae have different efficacy and toxicity responses regarding the removal of various pesticides. Most studies have reported the oxidative responses of microalgae in the presence of different pesticides concentrations. On the other hand, the morphology of microalgae alters in the presence of different concentrations of toxins impairing the photosynthesis process. Further reactions to the presence of pesticides in the environment include a decline in the cellular protein solubility and total antioxidant content, an increase in peroxidase and superoxide dismutase activities, a reduction in the transcription of photosynthetic genes and destruction of cell structure; however, the ability of microalgae resistance to specific concentrations toxins vary

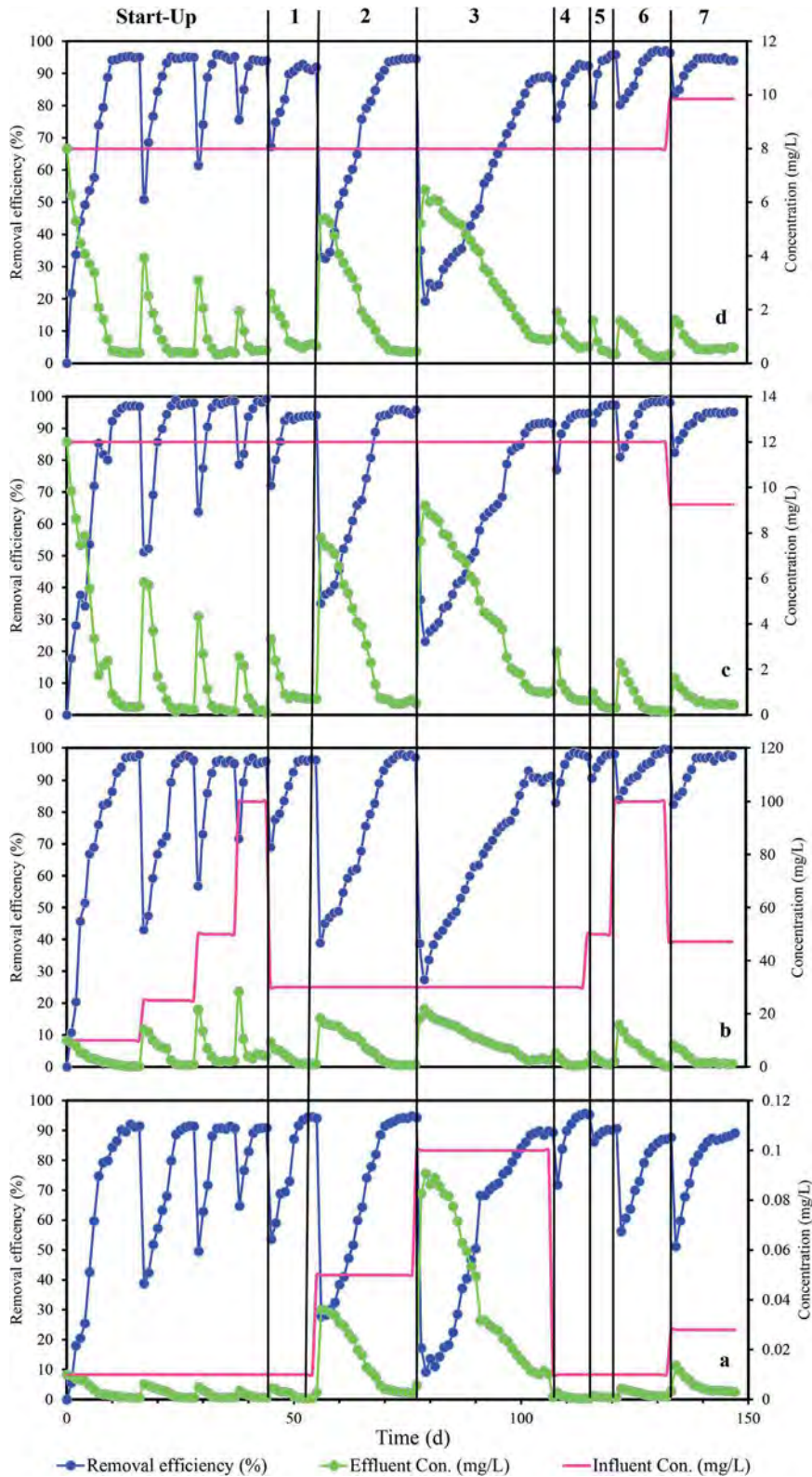


Fig. 2. Removal efficiency, influent and effluent a) atrazine, b) COD, c) PO_4^{3-} and d) NO_x profiles in the MPBR operated at different conditions.

depending on the conditions. Microalgae not only can bio-accumulate toxins, but also they can decompose these toxins in concentrations less than lethal levels (Friesen-Pankratz et al., 2003; Murdock et al., 2013). According to findings, it is evident that MPBR photobioreactor can remove simultaneously high concentrations of atrazine and target pollutants from aquatic environments. At the end of day 114 (phase 5), COD concentration increased to 50 ± 1.2 mg/L. The average of

contaminants removal efficiency after reaching the steady-state condition at HRT of 24 h in the MPBR is shown in Fig. 2 as a function of the influent COD concentration. As shown in Fig. 2, the average of atrazine removal efficiency at steady-state conditions for the influent COD concentrations of 30, 50 and 100 mg/L was 95.2%, and 87.6%, respectively, and for COD was 97.3%, 98.1%, and 99.2%, respectively. The standard deviation of less than 0.5% (Table 1) indicates highly

Table 3
Results of the biomass acclimation to atrazine biodegradation.

Acclimation run	time (d)	OLR (g/L-d)	COD removal efficiency (%)	ATZ degradation (%)	PO ₄ ³⁻	NOx
1st run	16	0.01	97.518	91.563	96.973	95.173
2nd run	12	0.025	97.054	91.328	97.913	95.157
3rd run	9	0.05	95.546	90.857	98.573	94.71
4th run	7	0.1	95.259	90.759	98.991	93.928

desirable and stable performance of the bioreactor regarding the removal of target pollutants during the steady-state conditions. The concentration of the influent PO₄³⁻ and NOx to the photobioreactor was 12 ± 0.3 and 8 ± 0.7 mg/L, respectively. Average of PO₄³⁻ removal efficiency at steady-state conditions for the influent COD concentrations of 30, 50 and 100 mg/L was 94.4%, 97.3% and 98.1%, respectively, and for NOx was 92.5%, 95.7%, and 97.1%, respectively. The effluent PO₄³⁻ and NOx concentration at the end of 132th day was 0.1 and 0.2 mg/L, respectively, which was much lower than the discharge standards. Some microalgae species have the ability to change their metabolic activity from autotrophic or heterotrophic, so they can use both organic carbon and inorganic carbon to fulfill their carbon needs. Based on previous studies, increased exposure to light has an influential role in the oxidation process and COD removal rate by algae-bacterial populations because of the microalgae mixotrophic lifestyle (Boelee et al., 2011; Luo et al., 2017). On the other hand, multifold growth of bacterial cells under light lamps in areas where density of algal cells is much higher indicating a strong correlation between the bacterial population and algal population and also their symbiosis (Maza-Márquez et al., 2017; Posadas et al., 2013). Consequently, the high COD removal rates found in this study (more than 99%) indicates the algal-bacterial symbiosis and the amplification of pollutants removal. The process of reducing the amount of COD in the biological treatment of wastewater using algae-bacterial biofilms begins with the massive destruction of organic molecules in the wastewater by bacteria and continues with direct absorption of the crushed molecules by algal cells (Luo et al., 2017). In Fig. 2c, the biological removal of PO₄³⁻ in MPBR is shown. Phosphorus is one of the essential elements for the growth and activity of microorganisms; however, microalgae can absorb so much of this element indicating that algae have the ability to accumulate phosphorus in their cells as polyphosphates. Phosphorus cellular absorption is strongly dependent on the concentration of organic substrate and this removal mechanism occurs more at higher concentrations of COD (Boelee et al., 2011; Praveen and Loh, 2016a). When the concentration of COD was 30 mg/L, the removal efficiency was 93.9% in the system. When COD concentration increased to 50 and 100 mg/L, the removal efficiencies enhanced to 97.3% and 98.1%, respectively. These results can be due to this fact that the absorption of phosphorus by microalgae is an active process and therefore requires a source of energy. Assimilation of phosphorus in algae systems typically depends on the amount of carbon's uptake and thus on the growth of algae (Boelee et al., 2011; Posadas et al., 2013; Praveen and Loh, 2016a). Fig. 2d shows the trend of NOx removal during the operation. It is clear that the function of the photobioreactor enhanced in terms of NOx removal when COD concentration increased. When COD concentrations were 30, 50 and 100 mg/L, the NOx removal efficiency was 92.5%, 95.7% and 97.1%, respectively. The concentration profiles of NOx and PO₄³⁻ were similar to each other. Although the removal process of NOx and PO₄³⁻ was generally similar in different phases, the efficiency of PO₄³⁻ removal in each phase was higher than NOx removal efficiency. Nevertheless, the efficiency of phosphorus removal never reached 100% that is because of phosphorus release potential due to biomass decomposition. Since the MPBR have not been already used for pesticides elimination and this is a newly-introduced method for atrazine removal, no researches have been conducted on this issue. However, a summary of the performance of the membrane photobioreactors, found in the

bibliography, is presented in Table 1S in the Supplementary data. Even so, the designed MPBR is highly efficient for nutrients and toxins removal. The efficiencies obtained in the current study concerning the removal of N and P was higher than those reported in previous studies (Table 1S). Typically, elimination of nutrients by the photobioreactors involves assimilation by microorganisms and chemical processes such as chemical combination of phosphorus and ammonium volatility. Both chemical processes are improved by environmental pH. In previous studies, it has been stated that when environmental pH is 7, chemical processes are ineffective regarding the removal of nutrients in the presence of microalgae (Gao et al., 2016; Luo et al., 2017; Maza-Márquez et al., 2017; Novoveská et al., 2016; Praveen and Loh, 2016a). Furthermore, natural pH is appropriate for microalgae growth. In the present work, pH of the environment was maintained at the range of 6.8–7.2 (Table 1); hence, the assimilation of nutrients by microalgae cells could be considered as the main cause of nutrients removal. On the 133th day, the MPBR reactor was operated with a real secondary effluent (Phase 7) and the results are presented in Fig. 2. The results showed a similar removal pattern during the experiments. Comparing the results of this study with other studies, it can be concluded that the efficiency of systems that use only microalgae for biological treatment of wastewater is less than systems that simultaneously use algae and bacteria that it shows the importance of algal-bacteria symbiosis. There was no accumulation of atrazine in the biofilm and loss of atrazine in the control reactor was negligible (> 10%). This shows that atrazine removal from the system has been as a result of biodegradation.

3.2. The effect of HRT on MPBR performance

Ensuring the cost-effectiveness of the operation of a system is very necessary. Therefore, the reactor volume and compression effectively affect the economic aspects of the operation phase. The appropriate HRT is the minimum required time for the reactor to have the desired efficiency, and finally the minimum volume and maximum compression are included (Metcalf and Eddy, 1991). To examine the effect of HRT on the performance of MPBR reactor, the effect of various HRTs from 6 h to 24 h was investigated while the concentration of atrazine was constant ($0.028 \pm 3 \times 10^{-4}$ mg/L). The results are summarized in Fig. 3. Although the reduction of HRT from 24 h to 12 h decreased the amount of pollutant removal, the MPBR function was again improved and returned to steady-state conditions after about 15 days. Then, HRT reduced to 6 h during the operation phase and the effluent concentration of pollutants was monitored. As can be seen in Fig. 3, the efficiency of pollutants removal suddenly decreased to less than 43%, 1 day after the change. However, with the continuation of the reactor operation, the results showed that the MPBR can quickly recover its function. Similarly, the removal of atrazine, COD, PO₄³⁻ and NOx reached to 88.5%, 97.5%, 94.4% and 93.7%, respectively, 21 days following hydraulic shock excretion when a stable condition was achieved. Recovery of MPBR reactor function after HRT decrease indicated that the MPBR reactor is resistant to loading rates and hydraulic shocks created by increasing the influent rate. Based on the results shown in Fig. 3, it can be inferred that the reduction of target pollutants removals at the beginning of any HRT decrease happen; but with continuation of the operation, the system restores and adapts itself to its new conditions and ultimately reaches stability. Selection of an appropriate HRT for the

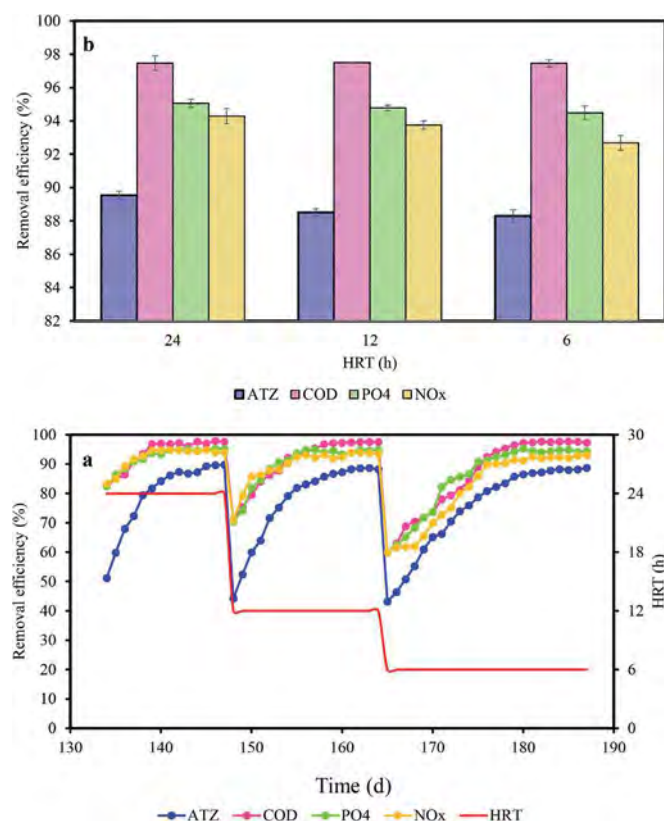


Fig. 3. Biodegradation of atrazine and COD, PO_4^{3-} , NOx removal in the MPBR at various HRT (atrazine = 0.028 mg/L; COD = 48 mg/L): (a) time-course and (b) mean steady-state results.

growth and cultivation of microalgae depends on a variety of factors, such as wastewater properties, targets pollutant, and climatic conditions (Boonchai and Seo, 2015; Gao et al., 2016, 2014). In the absence of toxin, shorter HRT resulted in the increase of nutrients loading and improvement of microalgae growth and cultivation (due to the high F/M ratio). However, the longer HRT resulted in an increase in the contact time of contaminants with the microorganisms and enhancements of the removal efficiency and system performance (Derakhshan et al., 2016a; Nasseri et al., 2014). Nevertheless, in the presence of toxic compounds such as atrazine, HRT reduction has led to an increase in the atrazine loading rate, which shocked the microalgae and disrupted the function of the system. When microorganisms adapted to the new conditions, the system reached stable condition and resorted to its optimal function. For different types of microalgae, an optimal HRT was investigated, but it is worth noting that the increase of HRT reduced the loading rates of organic nutrients compared to biomass inside the reactor, which leads to a reduction in the production of biomass due to lack of nutrients (Baghapour et al., 2013; Derakhshan et al., 2016a). Furthermore, excessive increase of HRT enhances the footprint of the treatment system. There are several strategies to prevent excessive HRT increase. One option is to keep species of microalgae that can quickly remove the existing pollutants during system operation. The faster and more stable removal of organic compound due to high concentrations of biomass can compensate the removal of organic compound in shorter HRTs. System Solids Retention Time (SRT) is equal to HRT for a conventional photobioreactor with suspended growth and a non-return biomass. However, the biomass is kept almost completely by the membrane of the photobioreactor in the MPBR system, which results in the use of photobioreactor with high biomass and short HRT. Further, it increased the acclimatization of the most slow-growing species in the system. The submerged membrane inside the MPBR enabled system to keep operation without exiting and washing microalgae cells (Boonchai

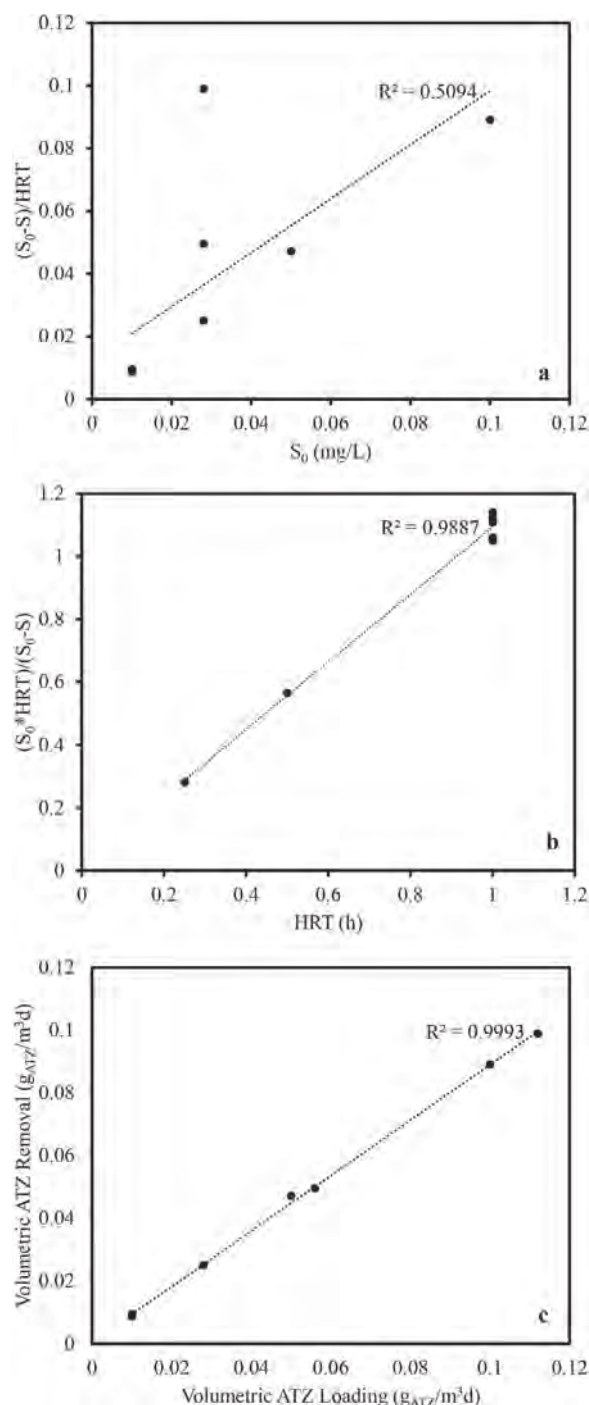


Fig. 4. Modeling of atrazine biodegradation in MPBR: a) First order model; b) Grau model; c) modified Stover-Kincannon model.

Table 4
Changes in the microalgae biomass composition in the MPBR.

	MPBR	Control
Carbohydrates (%)	26.3	24.2
Lipids (%)	51.7	39.8
Proteins (%)	4.1	3.3

and Seo, 2015; Gao et al., 2015; Praveen and Loh, 2016b). The results showed that HRT, in the process of wastewater treatment on the basis of microalgal-bacterial activity, can be reduced significantly by a MPBR system, which results in the reduction of the volume of the reactor. A

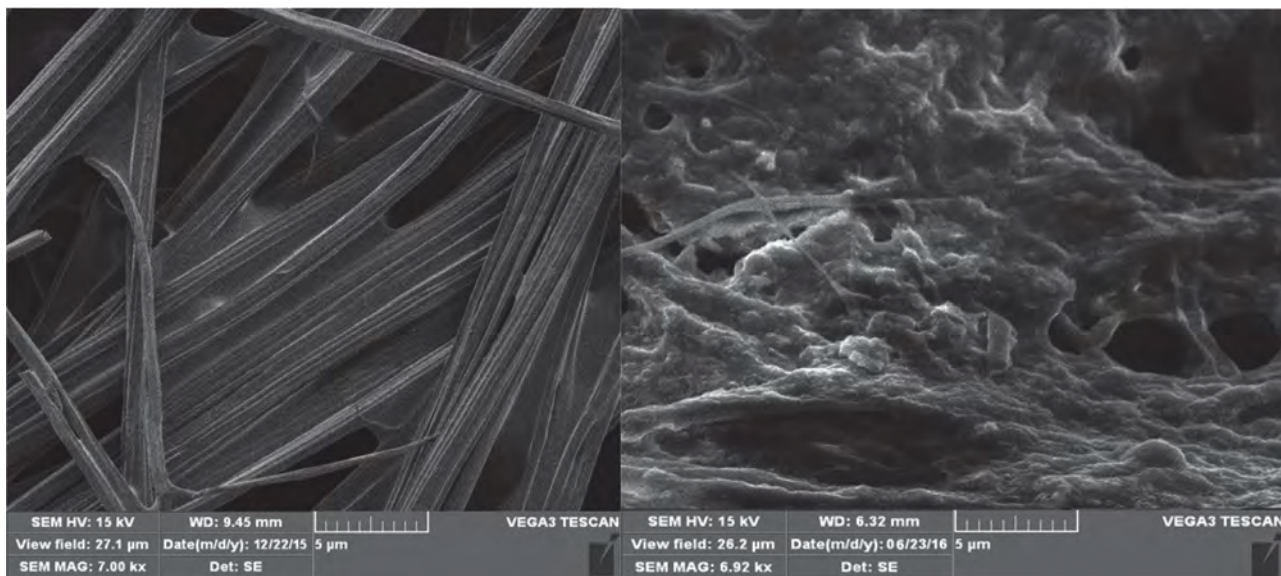


Fig. 5. SEM images of virgin surfaces of media (left) and media after biofilm formation (right).

better performance can be achieved by installing a submerged membrane filter in a photobioreactor to separate solid from the liquid, which can be useful both for the cultivation of microalgal biomass and for the enhancement of pollutants removal rate. Additionally, the microalgal biomass can be used to produce biofuel, fertilizer, etc. (Choi, 2015; Gao et al., 2014, 2015).

3.3. Modeling

Mathematical and experimental models are used to determine the relation between variables in order to evaluate experiments results (Baghapour et al., 2015). Moreover, these models are used to monitor and predict the performance of treatment unit and to optimize built a plant in Lab scale (Derakhshan et al., 2017b). Considering the design processes of biofilm, the removal rate of the substrate in the biofilm process is changed from limiting transfer reaction rate of the substrate from biofilm until limiting kinetics enzymes for substrate utilization and depends on the concentration of mass (Metcalf and Eddy, 1991). Simplified models consist of a small number of variables and can be used to determine the reaction kinetics. Among the models that are widely used to determine the reaction kinetics of biofilms in fixed and moving bed are including First order, Second Order (Grau) and modified Stover-Kincannon (Baghapour et al., 2013, 2015; Metcalf and Eddy, 1991). A brief explanation is brought in the Supplementary data. Using the Curve Expert software, coefficients can be derived. The first order, Grau and modified Stover-Kincannon models for atrazine removal in MPBR has been shown in Fig. 4. According to the correlation coefficients which were 0.509, 0.988 and 0.999, respectively, it can be concluded that first order and Grau models cannot be applied for predicting MPBR's performance with high degree of precision. Modified Stover-Kincannon model was obtained with correlation coefficients of 0.999 for atrazine removal, which shows a good degree of precision and can be used in the design of the MPBR reactors. The values of k and r_{\max} coefficients were determined 2.237 and $2.078 \text{ g}_{\text{ATZ}}/\text{m}^3 \text{ d}$, respectively. Results show that the MPBR bioreactor is more capable of removing atrazine from aquatic and modified Stover & Kincannon model has the better fit ($R^2 > 0.99$) for removing atrazine from aqueous environments. In a nutshell, this model is preferred for simulating the process of removing atrazine from aqueous environments.

3.4. The growth of biofilm and biomass in MPBR

At the beginning of MPBR operation, the microalgal-bacterial population and membrane surface bacteria were covered with a very thin layer after about 5 days, but membranes were still visible in some parts. Then, the green filament algae began to grow and reproduce on a thin film. On the 12th day, the biofilm on the membrane began to fall. This growth pattern was almost identical at all loading rates. However, at higher loading rates, a dark, very slack green biofilm was formed. Since the absorbance measurement did not show the actual amount of accumulated microalgal-bacterial biomass, the accumulated biomass was measured at the end of the reactor operation. The collected biomass was settled and suspended biomass, as well as the biomass attached to the surfaces, although not all the attached biomass could be completely recovered could be collected. Measurements were performed by absorbance and dry cell weight, and it was determined that the total biomass accumulated in MPBR reactor was greater than 6 g/L . The results suggested that the system has a high ability to grow and cultivated microalgae, which is in line with previous studies. In order to investigate the effects of the MPBR operating conditions on microalgae, the biomass composition of the microalgae from the MPBR was investigated, and compared with the control experiment. Table 4 summarized the lipids, proteins and carbohydrate of the microalgae in the control experiment, as well as in the MPBR. As show in Table 4 an increase in lipid content was due to the high nitrogen removal efficiency. The amount of biomass production was increased when the real secondary effluent was used to feed the system. Previous studies have demonstrated that the growth and cultivation of microalgae using real wastewater leads to a higher biomass production compared to synthetic wastewater, which can be due to richness of the real secondary effluent with the micronutrients, the essential nutrients, or their balanced and suitable composition for microalgae growth and cultivation (Praveen and Loh, 2016a, 2016b). To study the biofilm properties at the end of the experiments, a small piece of the membrane that the biofilm was grown on it was cut. SEM showed that the upper layer of biofilm is composed mainly of green filament microalgae, as shown in Fig. 5. Spherical microalgae were also enclosed in the Extracellular Polymeric Substances (EPS) protective layer. The membrane surface coating with EPS indicates that the formed biofilm was able to increase the resistance against water release at the membrane surface, which could reduce the flow flux during the long period of MPBR operation. The formed

biofilms had a good thickness and porosity, which increased the biological contact within target pollutants, which increased the contact between the atrazine-degrading microorganisms and improved the biodegradation process (Boelee et al., 2011; Derakhshan et al., 2017b).

4. Conclusion

Ability of the microalgal-bacterial system considered for aromatic pollutants biodegradation has been studied in part and in brief, but the catabolic pathways of decomposition of these compounds by microalgae are still widely unknown. In spite of the potential benefits of using microalgae in wastewater treatment, there is still no study on the evaluation of the performance of microalgal-bacterial bioreactors in atrazine treatment. We believe that this technology would have the ability to turn the wastewater treatment system from a single energy consumer into a pure energy producer process. In this research, the effects of atrazine and COD concentrations, and also HRT changes in were systematically identified in the removal of organic pollutants and nutrients from secondary wastewater effluent. The results shows that both HRT and initial concentrations are effective parameters on the cultivation of microalgal biomass and the removal of nutrients and organic pollutants. It was revealed that the growth and cultivation of microalgae is continuously possible for the production of biomass and the removal of contaminants by MPBR. MPBR is one of the best advances in treatment technologies for nutrients and organic pollutants elimination. Microorganisms are not only bioaccumulate pesticides, but also they can decompose these pesticides at concentrations lower than the lethal levels. However, the metabolic pathways for biodegradation of pesticides are still an unknown and unexplored area that should be investigated further.

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Competing interests

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.envres.2017.11.045>.

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